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Review

The composition-explicit distillation curve technique: Relating chemical analysis and physical properties of complex fluids☆

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ABSTRACT

The analysis of complex fluids such as crude oils, fuels, vegetable oils and mixed waste streams poses significant challenges arising primarily from the multiplicity of components, the different properties of the components (polarity, polarizability, etc.) and matrix properties. We have recently introduced an analytical strategy that simplifies many of these analyses, and provides the added potential of linking compositional information with physical property information. This aspect can be used to facilitate equation of state development for the complex fluids. In addition to chemical characterization, the approach provides the ability to calculate thermodynamic properties for such complex heterogeneous streams. The technique is based on the advanced distillation curve (ADC) metrology, which separates a complex fluid by distillation into fractions that are sampled, and for which thermodynamically consistent temperatures are measured at atmospheric pressure. The collected sample fractions can be analyzed by any method that is appropriate. The analytical methods we have applied include gas chromatography (with flame ionization, mass spectrometric and sulfur chemiluminescence detection), thin layer chromatography, FTIR, corrosivity analysis, neutron activation analysis and cold neutron prompt gamma activation analysis. By far, the most widely used analytical technique we have used with the ADC is gas chromatography. This has enabled us to study finished fuels (gasoline, diesel fuels, aviation fuels, rocket propellants), crude oils (including a crude oil made from swine manure) and waste oils streams (used automotive and transformer oils). In this special issue of the Journal of Chromatography, specifically dedicated to extraction technologies, we describe the essential features of the advanced distillation curve metrology as an analytical strategy for complex fluids.

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1. Introduction

This special issue of the Journal of Chromatography provides the opportunity to highlight the importance of separation/extraction processes in general, and how the specific techniques of chemical separations can be used to solve laboratory and industrial problems. The importance of separation processes cannot be understated, since nearly 40% of the cost of any chemical product is directly attributable to the separation processes used in their production [1]. These processes include distillation, extraction, adsorption, diffusion and zone refining, to mention just a few. For industrial applications, distillation has long been the dominant separation process, in terms of the overall number of units implemented, and in terms of total capital investment. The relative simplicity and efficiency, and the long term experience base makes distillation the first choice in the chemical processing industry, even when other methods might be viable.

Aside from the chemical production aspects, the dependence of separations techniques on intermolecular interactions has also provided the metrology to study chemical properties, and to determine how such properties relate to the constituents of mixtures. The application of chromatographic methods for physicochemical measurements, for example, has been well known for nearly 50 years [2]. Thermodynamic parameters measured by chromatography have been validated by other techniques such as spectroscopy and calorimetry. In a similar manner, we can use distillation as a measurement method, one that is especially applicable for complex fluids. Here, the relationship between composition on the one hand and vapor liquid equilibrium on the other (both controlling factors in distillation) furnishes us with a bridge between analytical chemistry and thermophysical property measurement [3,4].

Since complex, multi-component fluid mixtures vaporize over a range of temperatures, the only practical avenue to assess the vapor liquid equilibrium (VLE) is the measurement of the distillation or boiling curve [5]. The classical distillation curve of a fluid is a graphical depiction of the boiling temperature of the mixture plotted against the volume fraction distilled. This volume fraction is usually expressed as a cumulative percent of the total volume. One most often thinks of distillation curves in the context of petrochemicals and petroleum refining, but such curves are of great value in assessing the properties of any complex mixture [6–9]. Indeed, the measurement of distillation curves has been part of complex fluid specifications for a century (typically listed in specifications and data sheets as the fluid volatility), and they are inherent in the design and application of all fuels. Despite this importance, the standard methods for the measurement of such curves have been plagued with systematic uncertainty and bias, and an absence of any link to fluid theory [10]. This has lead many petroleum scientists and engineers to consider the measurement of distillation curves to be virtually meaningless, valuable only because everybody has done it the same way. Moreover, the standard metrology has always ignored the compositional aspects that are so important; distillation is really all about composition.

We recently introduced an improved method, called the composition-explicit or advanced distillation curve (ADC) metrology, as a means to characterize complex fluids [11–14]. The ADC approach addresses many of the shortcomings of the classical distillation methods described above. Most important, we incorporate a composition-explicit data channel for each distillate fraction (for both qualitative, quantitative and trace analysis). Sampling very small distillate volumes (5–25 μL) yields a composition-explicit data channel with nearly instantaneous composition measurements. Chemical analysis of the distillate fractions allows for determination of how the composition of the fluid varies with volume fraction and distillation temperature, even for complex fluids. These data can be used to approximate vapor liquid equilibrium of complex mixtures, and present a more complete picture of the fluid under study. The ADC approach provides consistency with a century of historical data, an assessment of the energy content of each distillate fraction, and where needed, a corrosivity assessment of each distillate fraction. Suitable analytical techniques include gas chromatography with either flame ionization detection (GC-FID) or mass spectral detection (GC-MS), element specific detection (such as gas chromatography with sulfur or nitrogen chemiluminescence detection, GC-SCD or GC-NCD), Karl Fisher coulombic titrimetry, refractometry, and Fourier transform infrared spectrometry (FTIR) [15,16].

Another advantage of the ADC approach is that it provides temperature, volume and pressure measurements of low uncertainty, and the temperatures that are obtained are true thermodynamic state points that can be modeled with an equation of state. In fact, we have used the ADC method to develop chemically authentic surrogate mixture models for the thermophysical properties of a coal-derived liquid fuel, a synthetic aviation fuel, S-8, and rocket propellants RP-1 and RP-2 [11–14,17–19]. The ability to couple the compositional data with the thermal data gives us access to numerous material dependent quantities, and the ability to relate them to the mixture volatility. We will illustrate this in the selected examples that follow.

1.1. Advanced distillation curve method

The apparatus and procedure for the measurement of the composition ADC have been discussed in detail elsewhere; only a brief description will be provided here [11,13]. The apparatus is depicted schematically in Fig. 1. The stirred distillation flask is placed in an aluminum heating jacket contoured to fit the flask. The aluminum jacket serves to integrate out temperature gradients in all but the vertical direction, in which direction a gradient must exist to provide mass transfer. The jacket is resistively heated, controlled by a model predictive PID controller that applies a precise thermal profile to the fluid [14]. Three observation ports are provided in the insulation to allow penetration with a flexible, illuminated borescope. The ports are placed to observe the fluid in the boiling flask, the vapor space at the top of the boiling flask, and the vapor in the distillation head (at the bottom of the take-off).

Above the distillation flask, a centering adapter provides access for two thermally tempered, calibrated thermocouples that enter the distillation head. Calibration is normally done with a triple point cell that can be traced to a NIST standard. One thermocouple (T1) is submerged in the fluid and the other (T2) is centered in the head at the low point of distillate take-off. Also in the head is a stainless steel capillary tube that provides an inert gas blanket for use with thermally unstable fluids. Distillate is taken off the flask with the distillation head, into a forced-air condenser that is chilled with a vortex tube [20–22]. The vortex tube is a device that produces a stream of hot and cold air from an ordinary shop air source. We use air as the cooling medium because it is easily controlled, and it avoids the problems associated with a water flow. Water cooled condensers can cause glassware cracking due to the high heat capacity of water, and always involve the potential for leaks.

Following the condenser, the distillate enters a new transfer adapter that allows instantaneous sampling of distillate for analysis. The flow path of the distillate is focused to drop into a 0.05 mL "hammock" that is positioned directly below the flow path. A crimp cap or screw cap fixture is incorporated as a side arm of the adapter. This allows a replaceable silicone or Teflon septum (of the type used for chromatographic automatic sampler vials) to be positioned in